TECNOLÓGICO DE MONTERREY

Departamento de Ingeniería Química

TECHNICAL REPORT

COMPARATIVE RISK STUDY FOR NATURAL REFRIGERANTS

Presented by:

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Prepared for:

PANAMÁ GREEN INNOVATIONS, S.A.

Monterrey, Nuevo León, Mexico **June 10, 2009**

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Background Information

Panama Green Innovations, S.A. manufactures natural refrigerants of various formulations based on oil hydrocarbons. Due to their formulation, these mixtures of refrigerants present flammability properties that correspond to the components comprising the mixtures. Nevertheless, the company ensures that the correct use of these refrigerants will not present any additional risk with regard to refrigeration equipment.

Panama Green has requested that Tecnológico de Monterrey simulate various potential risk scenarios involving natural refrigerants, and that these events be compared with risk situations that are commonly present in the various areas where refrigeration equipment is used: residential, commercial and industrial applications.

Applications involving natural refrigerants supplied by Panama Green that will be analyzed in this study are as follows:

1. Mini split-type air conditioning equipment with a cooling capacity of 2 tons
2. Central air conditioning equipment with a cooling capacity of 5 tons
3. Household refrigerator, capacity of 18 cubic feet
4. Chiller-type refrigeration equipment (water cooler)
5. Cold room refrigeration equipment

For each of these applications, the possible effect of a total and sudden refrigerant leak will be analyzed, reviewing any potential toxicity and explosivity conditions. In the event that the proposed scenario has the potential to generate an extraordinary risk event (explosion or fire), a simulation of the event will be conducted in order to determine the magnitude of damage.

For the purposes of comparing risks, baseline cases will be proposed that are commonly found in residential, commercial and industrial settings. The baseline cases include the simulation of risks present due to the use of Natural Gas or LP Gas in equipment such as stoves, heaters and storage equipment such as stationary tanks and cylinders. For industrial applications, the baseline case of an acetylene cylinder for welding will also be used.

Study Objective

The objective of this study is to estimate the magnitude of risk events related to a total and sudden leak of natural refrigerant contained in five different refrigeration applications, and to compare the identified effects, with risk situations commonly present in the areas of application of these refrigerants, i.e. household, commercial and industrial applications.

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Methodology

This section describes in general terms the methodology used to carry out risk assessments for each of the scenarios, as well as the manner in which the results will be compared with baseline cases. A description of the cases to be studied, the physical properties of the relevant substances, as well as the models used to assess the explosion, fire and toxic substance exposure risk scenarios, have been included.

Cases simulated

As was stated above, five cases involving the use of natural refrigerants will be studied. They will be compared with common situations (baseline cases). These cases and the baseline cases are described below.

Case 1. Mini split-type air conditioning equipment with a cooling capacity of 2 tons

This is an application intended for residential use (it may be used in offices as well) and the installation of this equipment includes a condenser unit and an evaporative unit. The condenser unit is typically installed on the roof of the residential house (outside of the room to be cooled), while the evaporative unit is installed in one of the interior walls of the room to be cooled.

An air conditioning unit of this size (2 tons cooling capacity) is typically used for rooms measuring approximately 32 m^2 with a height of 2.5 m, depending on the specific details of the room (number of windows, solar radiation, number of persons, among others).

Based on the data supplied by EuropaFrost, this type of unit uses a load of 1 Kg of HCR 410 refrigerant.

Case 2. Central air conditioning equipment with a cooling capacity of 5 tons

This equipment is commonly used in commercial applications. It consists of a cooling unit that is installed on the roof of the area to be cooled. The air injection and extraction ducts are connected to the area to be cooled. This unit uses 2.5 Kg of HCR 410 coolant from Panama Green and it is able to cool an area of 80 m^2 by 2.5 m in height.

Case 3. Residential refrigerator with a capacity of 18 cubic feet

This case involves a refrigerator for common use with a capacity of 18 cu. ft. This equipment is a conventional refrigerator that uses 0.06 Kg of natural RHC 134 refrigerant from Ecofreeze. This equipment is typically used in the kitchen area of a residential home.

Case 4. Chiller-type cooling equipment (chilled water)

This application is commonly used in building air conditioning equipment. The cooling system normally is installed on the roof of the building, and it is used to cool water, which is sent via piping to the cooling units located in the various areas to be cooled. The refrigerant in this type of equipment is only located in the water cooling system. The equipment to be simulated contains [illegible] HCR 410 refrigerant.

Case 5. Cold room refrigeration equipment

This [illegible] is used in commercial or industrial facilities where refrigerated rooms are required. The typical application is perhaps the storage of perishable food, whether it is refrigerated or frozen. Equipment "a" with these features to be simulated is rated at 2 HP for cold rooms with a surface area of between 10 m^2 and 16[m]^2 and measuring 2.5 m in height, depending on the specific [illegible] in question. The refrigeration equipment is divided into two parts; the compressor-condenser unit that is installed outside of the cold room, in a machinery area, and the evaporative unit that is installed inside the cold room. This equipment uses 2 Kg of HCR 410 natural refrigerant.

Baseline Cases

Baseline cases are possible risk scenarios involving household, commercial and industrial facilities, with regard to which the risks involved in Cases 1 through 5 described above are compared. The scenarios to be analyzed as baseline cases and that are compared in relation to the scenarios of Cases 1 through 5 are described below.

Baseline Case 1: Household stove using LP or natural gas

This case analyzes the scenario of an accidental gas leak due to one or several burners being open. The potential consequences of such a leak are evaluated: toxic environment and explosive environment. In this scenario, a kitchen size of 2 m x 3 m x 2.5 m was used as the basis for calculations. This baseline case serves as the framework for comparison for the risk events involved in the use of a household refrigerator with RHC 134 natural refrigerant (Case 3).

Baseline Case 2: LP or natural gas leak from a household heater

This case compares the risks involved in an HCR 410 refrigerant leak from the evaporator unit of 2-ton mini split cooling equipment (Case 1). Due to a leak of this type releasing refrigerant into a dwelling, the event is compared to the possible scenario of having heating equipment that burns LP or natural gas. The scenario described for this baseline case is that of a leak of gas fuel from the heater to the point of reaching explosivity limits within the dwelling. The dwelling considered in this case will have a surface area of 32 m^2 with ceiling height of 2.5 m. These are the recommended dimensions for the use of mini split cooling equipment with a capacity of 2 tons.

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Baseline Case 3: Stationary LP gas tank

This case considers a common size of stationary tank for the application in question (residential use: 120 l to 180 l or commercial use: 300 l) holding LP gas. Although larger stationary tanks exist, the comparison will only be carried out with these tanks. If the magnitude of the risk event involving these tanks exceeds the magnitude of the events where refrigerants are involved, it is not necessary to evaluate equipment with greater capacity, since the magnitude of the event would be even greater. For these installations, an accidental leak of all the material is considered, and the potential damage from explosion of the gas cloud and the fire occurring subsequent to the explosion (fireball) was analyzed. These tanks are typically installed on the roof of the building.

Baseline Case 4: 30 Kg LP gas cylinder for residential use

Similar to the stationary tank, this case assesses an accidental gas leak, and the consequences of explosion and fire are explored. Unlike stationary tanks, these types of cylinders normally are located at floor level and in some cases, they may be inside the same dwelling. These tanks are recommended to be installed outside of residential buildings.

In all cases and baseline cases, evaluation involved whether the event provides situations that represent a health risk due to exposure to toxic substances, whether the concentrations reached fall within substance explosivity limits, and if so, any effects due to explosion of the material.

Properties of the substances involved

This section presents the physical and toxicological properties of the substances involved in this study.

To evaluate toxic situations, the IDLH (Immediately Dangerous to Life and Health) value for each substance will be used. This value is reported by the United States National Institute for Occupational Safety and Health (NIOSH). It is used as a standard for determining toxic substance exposure limits.

In order to determine the possible creation of explosive environments, exclusivity limits reported for the substances in question will be used. In the event that the substance in question is a mix of various compounds, an estimate will be prepared based on the proportional quantity of the components comprising the mixture.

The table below presents the physical and toxic properties of HCR 410 and RHC 134 refrigerant that are relevant for this study. These properties were provided by the company Panama Green. The names of the components, as well as the formulation of these refrigerants, are the property of Panama Green and are not presented in this study.

Table 1. Relevant physical and toxic properties for natural refrigerants

Property	**Units**	**HCR 410**	**RHC 134**
Gas density (25°C)	Kg/m^3	2.4107	2.4107
Lower flammability limit	% v/v	2%	2%
Upper flammability limit	% v/v	9%	9%
IDLH	ppm (v/v)	2100	2100
ΔH combustion	Kcal/Kg	11,986.4	11,986.4

These data were provided by Ecofreeze and are valid for Eco22 and Eco134 refrigerants.

The properties of the substance involved in the baseline cases were obtained from data reported on material safety data sheets (MSDS) or they were estimated based on the composition of the mixture and the properties of their pure components. Table to present the properties for natural gas, LP gas and acetylene. It must be noted but in none of these cases are the mixtures are their components deemed toxic to health, however asphyxiating gas properties (oxygen displacement) and the risk of explosivity are present. In these cases, NIOSH establishes the IDLH levels as 10% of the lower explosivity limit (LEL) expressed as parts per million. The values presented for IDLH comply with this recommendation, since the substances are not toxic. The calculation report estimating the properties of the mixtures is reported in Appendix 1 to this report, as well as in the material safety data sheets (MSDS) for natural gas, LP gas and acetylene.

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Table 2. Properties of substances used in Baseline Cases

Description	Units	Natural Gas	LP Gas	Acetylene
Components				
Methane	% vol.	88	-	-
Ethane	% vol.	9	-	-
Propane	% vol.	3	60	-
Butane	% vol.	-	40	-
Acetylene	% vol.	-	-	100
Lower Explosive Limit (LEL)	% vol.	4.73	1.98	2.5
Upper Explosive Limit (UEL)	% vol.	14.6	9.06	100
IDLH	ppm (volume)	4733	1980	2500
Gas density @ 15.5°C	Kg/m^3	0.764	2.516	1.1716 @ 0°C
Liquid density	Kg/m^3	540	554	-
ΔH combustion*	Kcal/Kg	11,872.4	11,015.4	11,525.3

*estimated using data for pure components reported by Yaws C.L. (1999)

Method for assessment of explosion events

The estimate of damage produced by the explosion of combustible material may take various forms. The method commonly used and accepted for estimating the effects of a shockwave produced by explosion of a combustible material (for example a cloud of combustible gas) is the TNT method. This technique consists of determining the equivalent mass of TNT that would cause an explosion similar to that of the material in question and assessing the potential damage with respect to the distance from the center of the explosion. This is achieved by comparing the energy released by the sudden combustion of TNT and that of the combustible material. A detailed description of the TNT method is reported by Frank P. Lees (1996) or in the CCPS-AICHE guide (2000).

During an explosion of a combustible gas, only between 2% and 15% of a combustible material releases energy that is transformed into the shockwave produced by the explosion. The percentage depends on the reactivity of the combustible material; common combustible gases have a reactivity value of 5%, while acetylene is highly reactive and has a reactivity value of 15% (Lees F.P., 1996).

Once the equivalent quantity of TNT has been estimated, the distances at which the corresponding overpressure values occur can be determined. These values are determined based on the type of damage to be assessed. For example, it is known that for overpressure values of 1 psi or less, there is a 95% probability of no severe damage occurring. However, between 0.5 and 1 psi, it is very probable that window glass will break. Similarly, for overpressure values greater than one PS major damage to facilities is expected (CCPS, 2000).

For this study, we will use an overpressure reference value of 1 psi to determine high- and low-risk zones. In addition, the distance at which a pressure value of 10 psi or greater occurs, and where damage is deemed to be catastrophic, will be reported.

Evaluation of a fire event

Techniques for evaluating risks produced by fire involving a combustible material focus primarily on the risk posed to individuals by fire produced by the radiated heat, focusing on the probability of serious burns occurring. Although several classes of fire exist, the fire the correspondence to the type of materials corresponding to this study is a "fireball". This fire occurs when a gaseous combustible material leaks and forms of cloud of combustible material, which reaches exclusivity limits and catches fire. In this scenario to practically [illegible] processes occur. First a shockwave is produced by the sudden expansion of the gases (the effects of this event are assessed using the TNT method described above). Following the explosion, the material contained in the fuel cloud combusts, creating a large ball of fire (thus its name) that radiates heat in the surrounding area. The magnitude of heat radiated varies based on the distance from the fireball, and it is possible to calculate it using heat transfer and radiation concepts, and several empirical equations created for these cases (CCPS, 2000).

Once the radiation values at various distances from the source have been determined, the distances for the high-risk and buffer zones are calculated. It has been observed that a human being may be exposed to heat radiation of 1.6 kw/m^2 for long periods without experiencing burns. The distance to the source at which radiation of 1.6 kw/m^2 or less occurs is known as the minimum buffer distance. Between 1.6 and 4 kw/m^2, an individual will experience pain from 20 sec. of exposure, and possible second-degree burns from longer exposure periods. For radiation of 9.5 kw/m^2, an individual will feel pain from exposure lasting 8 sec. and will present second-degree burns from exposure lasting 20 sec. (Lees F.P., 1996). Zones presenting radiated heat values of between 4 kw/m^2 and 9.5 kw/m^2 are deemed to be high-risk zones. At the distance where heat radiation greater than or equal to 9.5 kw/m^2 occurs, it is not likely that individuals can be rescued alive. The distances at which 1.6 kw/m^2 and 9.5 kw/m^2 of radiated heat occurs have been estimated in this study as reference values for comparing the various cases.

Assessment of toxicity

The assessment of risks due to exposure to toxic substances is used to determine levels of exposure to certain materials that do not present a risk to human health, either chronically or acutely. There are a large number of parameters for defining and determining levels of health risk due to exposure to toxic substances, however due to the fact that all the substances covered by the study are not in and of themselves toxic substances, only the IDLH value reported by NIOSH will be considered.

For non-toxic combustible gases such as those present in this study, NIOSH establishes an IDLH of 10% of the Lower Explosive Limit (LEL) value in parts per million (NIOSH, 1994).

This study compares the concentration of gases produced by simulated refrigerant leaks to the IDLH value, since there is no health risk if the concentration obtained does not exceed the IDLH value. In the event that any value exceeds the IDLH, it does not necessarily mean that there is a toxicological risk (since these gases are not toxic), but rather, NIOSH considers there to be a possible risk to individuals when combustible gas concentrations in the air may be within the explosive limits (when reaching the IDLH, we are at 10% of the LEL and NIOSH considers it risky to work at levels greater than or equal to this value). Nevertheless, this does not mean that a concentration of these gases equal to or in excess of the IDLH presents an immediate toxicological health risk.

Results and Analysis of Results

The results obtained from the simulations of risk events for Cases 1 to 5 and the Baseline Cases are presented below. The results are presented for each Case, and they are compared to the corresponding Baseline Cases. An interpretation and discussion of the results obtained and their implications are also presented.

All the discussions of the results and the corresponding interpretation are prepared with the assumption that the facilities and equipment were maintained in acceptable conditions and that they were used in accordance with the purposes for which they were designed.

The calculations required for each of the modeled risk scenarios were conducted in accordance with each of the methods briefly described in the methodology section. These methods were detailed in the volume, "Guidelines for Chemical Process Quantitative Risk Analysis (CCPS, 2000), the reference work that was used to general [sic: possible typo for "to create" the Excel and Visual Basic forms used for the calculations. Appendix 2 includes the tables and graphics generated using these computer tools.

Case 1: Mini split-type air conditioning equipment with a cooling capacity of 2 tons

As was noted in the methodology section, this equipment comprises two units: One condenser unit that is installed on the roof of the residence to be cooled, and an evaporative unit that is installed within the dwelling to be cooled. Due to the fact that the refrigerant circulates throughout the condensation-evaporation circuit, two scenarios were considered regarding a refrigerant leak: The first scenario is a refrigerant leak from the evaporation unit, where all the refrigerant (1 Kg of HCR 410 leaks into the residence). The second scenario is a total leak of the refrigerant from the condenser, i.e. outside of the residence, located on the roof.

For the first case (total leak from the evaporator), the following risks due to accumulation of gas within the residence were identified: 1) the risk that the Lower Explosive Limit is reached and that an explosion event may occur; and 2) the risk that an environment will be achieved with refrigerant concentrations in excess of the IDLH, creating a situation that is unacceptable per NIOSH regulations.

Based on the cooling capacity of the mini split equipment (2 tons), a residence with surface area of 32 m^2 and a height of 2.5 m was defined, for a total volume of 80 m^3. Based on this volume, and given that the volume of HCR 410 refrigerant held by this system is 1 Kg (density of 2.4017 Kg/m^3), it may be determined that an air volume of 197 m^3 is required to have a refrigerant concentration equal to the IDLH value. Since the volume of the dwelling is only 80 m^3, the concentration of refrigerant in the dwelling will exceed the established IDLH level. Nevertheless, we recall that the gases considered in this study are not toxic and that the IDLH level is only a safety reference level established by NIOSH.

Similarly, the quantity of air necessary to reach the Lower Explosive Limit (LEL) may be estimated. The HCR 410 refrigerant has an LEL of 2% v/v, therefore in order to achieve this level, 20.7 m^3 of air is required. The volume of air in the residence is almost four times greater than the level required to create an explosive environment situation, therefore it has been concluded that a total leak of refrigerant does not present an explosion risk situation.

Although we have already seen that an explosive environment is not feasible in the entire residence, a situation wherein the refrigerant gas accumulates in a certain section of the residence and reaches the LEL is possible3, therefore although that limit will not be reached in the entire residence, an explosive event involving 1 Kg of HCR 410 will be simulated.

So, in order to be able to compare this risk event, we are going to consider one of the baseline cases that considers a natural gas or LP gas leak. This scenario is feasible if we consider that the residence may have a gas heater and that it may for some reason have a leak. The flow of leaking gas from the heater will be deemed to be equal to the estimated consumption flow of a gas heater. This flow rate depends on the type of gas used (natural or LP gas) and the capacity of the heater. These values are reported (Nacobre, 2009) to be in the range of 0.27 to 0.84 m^3/hr. for natural gas and between 0.1 and 0.32 m^3/hr. for LP gas.

Unlike the gas contained in the mini split air conditioner, and natural gas or LP gas leak from the heater has the potential of reaching the LEL (or ILDG) concentration, since the gas supply is maintained until the leak is detected, or until a risk event occurs. For this study it was considered that a gas leak would continue until reaching the LEL value, then causing an explosion event. So, for natural gas, two. 05 Kg is required to reach the LEL of four. 73%, while for LP gas, two. 826 Kg of gas is required to reach the LEL of one. 98%. It must be noted that LEL values are reported in percent by v that is, the volume of combustible gas out of the total volume of the residence, multiplied by 100. Figure One shows the comparative results of simulations for the explosion event for refrigerant, natural gas and LP gas. The distances at which an overpressure of 10 psi (catastrophic damage) and overpressure of 1 psi (considerable damage) would occur are presented.

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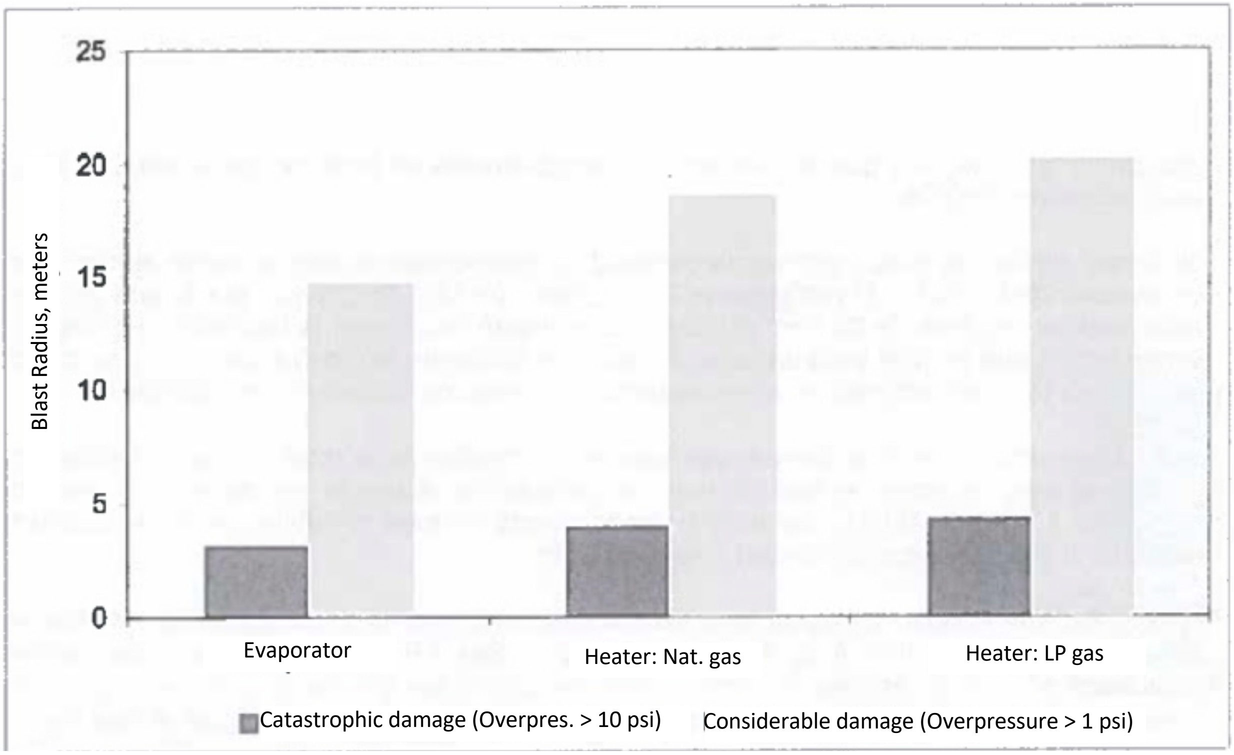

Figure 1. Comparison of the blast radii for a combustible gas leak explosion event in a residence of 32 m^2. A refrigerant leak explosion case does not reach the LEL, therefore it is unlikely that the event would occur, nevertheless the results are presented for purposes of comparison with other cases.

Figure 1 shows us that if a leak event and refrigerant gas explosion occurs, the areas affected are smaller than those that would be produced by a natural gas or LP gas leak explosion involving a heater. Additionally, it is important to stress that the volume of refrigerant contained in the mini split equipment is not sufficient for a residence of 32 m^2 or more to reach the Lower Explosive Limit (LEL). This is not the case in scenarios involving a natural gas or LP gas leak from a residential heater.

In the event that a refrigerant leak occurs from the condenser unit (typically located on the roof of the area to be cooled), calculations similar to those described above are carried out. In this case, given that the condensation equipment is outside and in a ventilated area, it is difficult for the refrigerant gas leak to cause HCR 410 concentrations in the air that exceed the IDLH and LEL levels. Nevertheless, like in the case of the evaporator, the refrigerant explosion blast radii will be compared to possible scenarios in a residential dwelling. The possible scenarios selected involve the presence of a stationary residential tank for LP gas, or alternatively the presence of an LP gas tank like those installed in residences where there is no stationary tank. The primary difference between these two scenarios is the capacity of the tank and location. Normally, stationary tanks have a higher capacity than gas cylinders, and they are typically located on the roof of houses (primarily for security reasons). Nevertheless, LP gas cylinders generally are placed at ground level outside of houses (laundry areas or patios, etc.), although it is common to see them installed inside of houses (a high-risk situation).

The capacity values for these tanks were selected from among the smallest volumes commercially available. Thus, the capacity for a residential dwelling is 120 L and the LP gas cylinder capacity considered is 30 Kg.

For each of the cases (refrigerant leak, LP gas leak from a stationary tank and cylinder), a total leak of the material and a subsequent explosion were simulated. The areas affected with catastrophic damage and significant damage are presented in Figure 2.

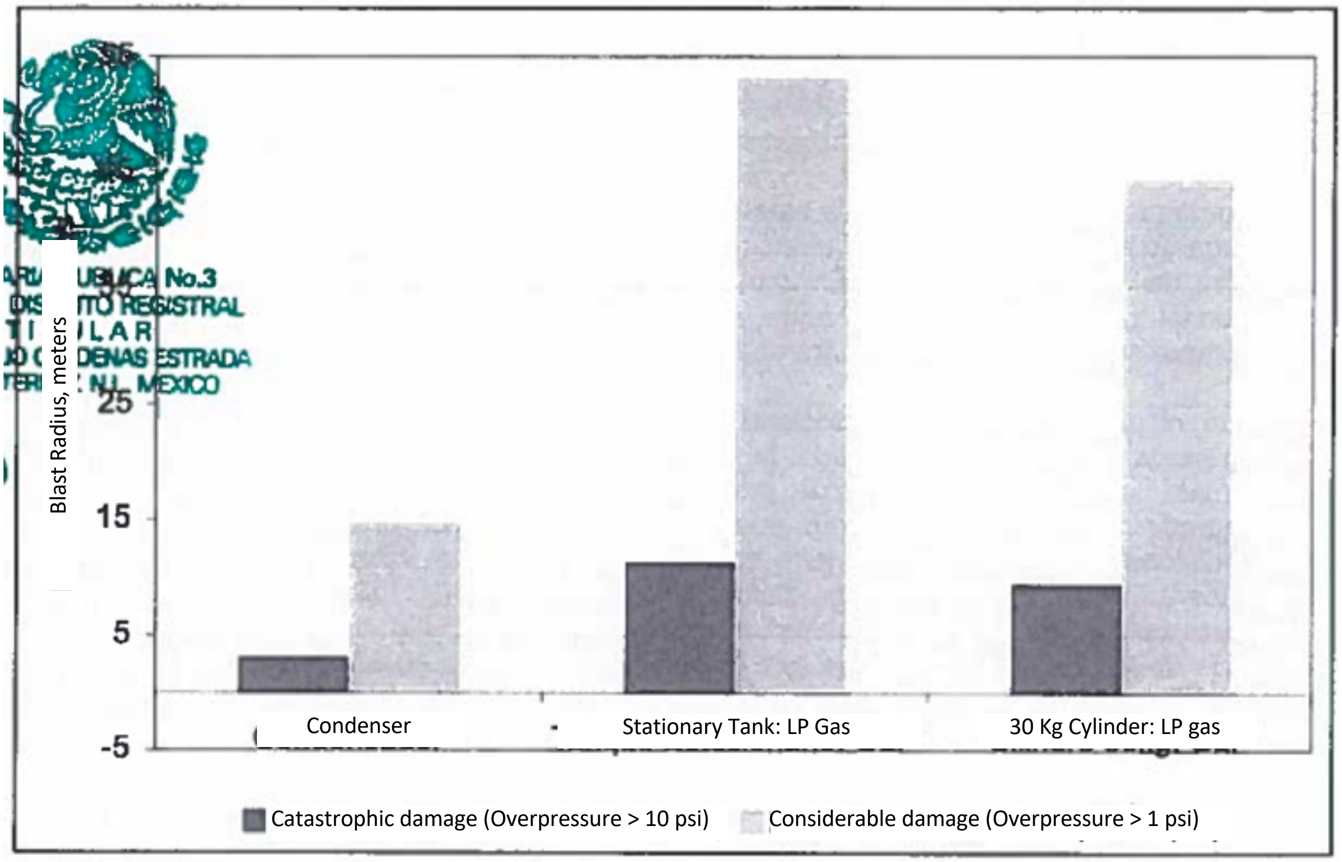

Figure 2. Blast radii resulting from explosions in cases of HCR 410 refrigerant leak cases from a condenser unit, total leak of LP gas from a stationary 120 L tank and total leak of LP gas from a 30 Kg cylinder.

Again, the blast radii from possible explosion events involving a stationary tank or an LP gas cylinder are significantly greater than the radii in the event of a refrigerant explosion.

It must be clarified that explosion events involving refrigerant and LP gas contained in the stationary 120 l tank are improbable events if this equipment is installed on the roof of a residence and out of doors. That is not the case for a 30 Kg cylinder, which even if it is installed correctly outside of a house and with good ventilation, due to the fact that they are continually being handled (connecting and disconnecting them), leaks are frequent and it is possible that the gas may enter and accumulate in an enclosed area, making an explosion event more probable. Additionally, given that they are installed at ground/floor level, the destructive consequences for the building are greater.

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Case 2: Central air conditioning equipment with a cooling capacity of 5 tons

Central air conditioning equipment is commonly used in commercial areas, although this equipment may be installed in residential buildings. This equipment is normally located on the roof of the building, where the condenser unit and the evaporator are located. Air in the conditioned area circulates through ducts from and to the cooling system. The equipment to be considered in this case has a cooling capacity of 5 tons and it contains 2.5 Kg of HCR 410 refrigerant. This equipment may be used to cool a surface area of approximately 80 m2 with a height of 2.5 m.

Given that this equipment is typically located on the roof of the building, a refrigerant leak event is compared with LP gas leak events from a stationary tank or from a 30 Kg LP gas cylinder. In this case, given that the typical scenario is a commercial installation, for example a restaurant, the selected stationary tank is 180 L, which is a medium-sized tank for this type of application.

From a toxicity point of view, if the refrigerant leak occurs in the equipment and the refrigerant leaks outside, the possibility that IDLH levels will be reached is minimal. Nevertheless, there exists the possibility that the refrigerant leak will occur in an evaporator and that the refrigerant may be injected by the system of ducts into the air conditioned area. Considering this scenario, the volume of air necessary in order for the leaked 2.5 Kg of HCR 410 refrigerant to reach IDLH levels (2100 ppm v/v). The result of this calculation is that approximately 494 m^3 of air is required in order to achieve IDLH levels. The volume of air available in an 80 m3 area with 2.5 m of height is 200 m^3, therefore IDLH will be exceeded if the refrigerant enters the air conditioned area.

Similarly, in order to see whether the Lower Explosive Limit (2% v/v) can be reached in the event of a refrigerant leak within the building, calculations show that approximately 52 m3 is required to achieve it, therefore the volume of 200 m3 exceeds this value by nearly a factor of 4, making an explosion event within the building unlikely.

Like for Case 1, although the explosion event is unlikely, an explosion event caused by a total refrigerant leak was simulated and its effects were compared to the explosion events of a stationary tank with a capacity of 180 l of LP gas and with an explosion of an LP gas cylinder with a capacity of 30 Kg. Figure 3 presents the comparative results of the area impacted by a leak and explosion in the aforementioned scenarios.

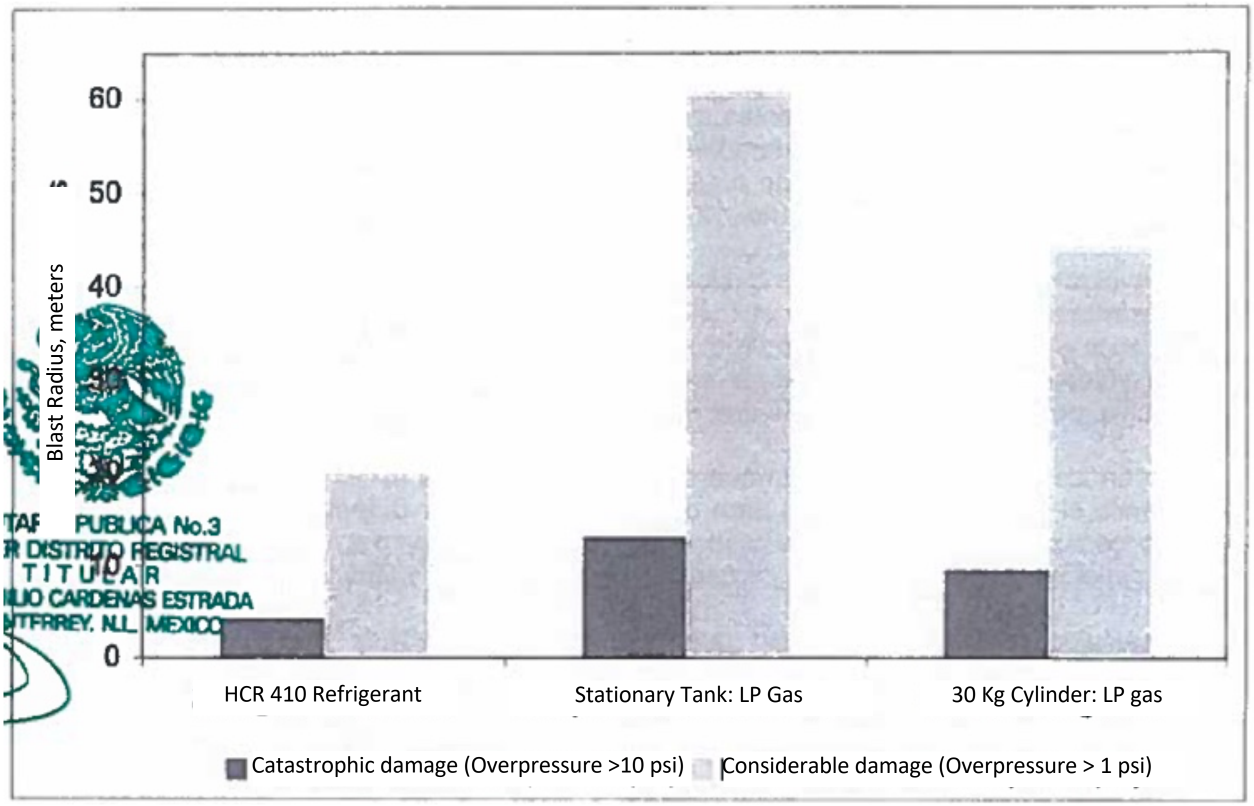

Figure 3. Blast radii for leak events and explosion involving: 5TRxxx central air conditioning equipment with 2.5 Kg of HCR 410 refrigerant, stationary tank with a capacity of 180 L for LP Gas and a 30 Kg cylinder for LP gas.

Figure 3 shows that in the event of an explosion due to a refrigerant leak, the blast radii are less than those that would be caused by LP gas leak and explosion events. The explosion of a stationary 180 L LP gas tank has a catastrophic damage blast radius of approximately 13 m, compared to 4 m for an event involving HCR 410 refrigerant. This approximate 3:1 proportion is maintained for blast radii with considerable (moderate) damage for these same two events. The case of a 30 Kg cylinder is improbable, since this type of equipment is not frequently present in commercial locations (at least those that may have centralized climate control), however this scenario was used for purposes of comparison. A single 30 Kg LP gas cylinder may cause explosion blast areas double those that are predicted for the refrigerant.

Case 3. Residential refrigerator with a capacity of 18 cubic feet using RHC 134 refrigerant

These types of equipment are typically used within kitchen areas of residential dwellings, therefore as discussed in the methodology section, the simulated scenario for this case is a total leak of the refrigerant into a small to medium kitchen, measuring 3 m x 2 m with a height of 2.5 m. The consequences of the refrigerant leak event are compared to the consequences of a natural gas or LP gas leak from other equipment commonly found in kitchens, i.e., a stove.

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A kitchen with the aforementioned dimensions has a volume of 15 m^3 and the total leak of refrigerant requires approximately 12 m^3 of air to reach IDLH levels, therefore in this leak scenario, the IDLH level is not reached, although the concentration level will be very close (12 m^3 vs. 15 m^3 available).

In order to assess the explosion risk case, we performed a similar calculation to see if the refrigerant lek is capable of reaching the Lower Explosive Limit (LEL) in the kitchen. In order for the LEL to be reached in the kitchen, a volume of approximately 1.25 m^3 is required, therefore the kitchen volume of 15 m^3 exceeds the volume [required] to yield an explosive environment by a factor of 12, therefore an explosion event is unlikely.

As in the prior cases, although the LEL is not reached in the total volume of the kitchen, the explosion event was simulated in order to determine potential damage and to be able to compare damage versus the baseline case. In this case, the refrigerant explosion event is compared to the probable natural gas and LP gas leak and explosion scenarios involving a stove.

Calculations carried out show that a stove burner that is leaking or that is accidentally left open reaches the Lower Explosive Limit in a 3x2x2.5 m kitchen in 4.2 hours for natural gas and 1.75 hours for LP gas. These values were estimated based on the gas flow reported for commercial stoves (Nacobre, 2009). If the leak comes from the oven, or from several open burners, the time to reach explosive levels is reduced significantly. For example, an oven leak reaches explosivity levels in 1.5 hours for natural gas and 0.65 hours for LP gas.

Based on the leak data for each of the proposed scenarios for this case, the blast radii were determined for each explosion event. Figure 4 presents the blast radii (catastrophic and moderate) for each case.

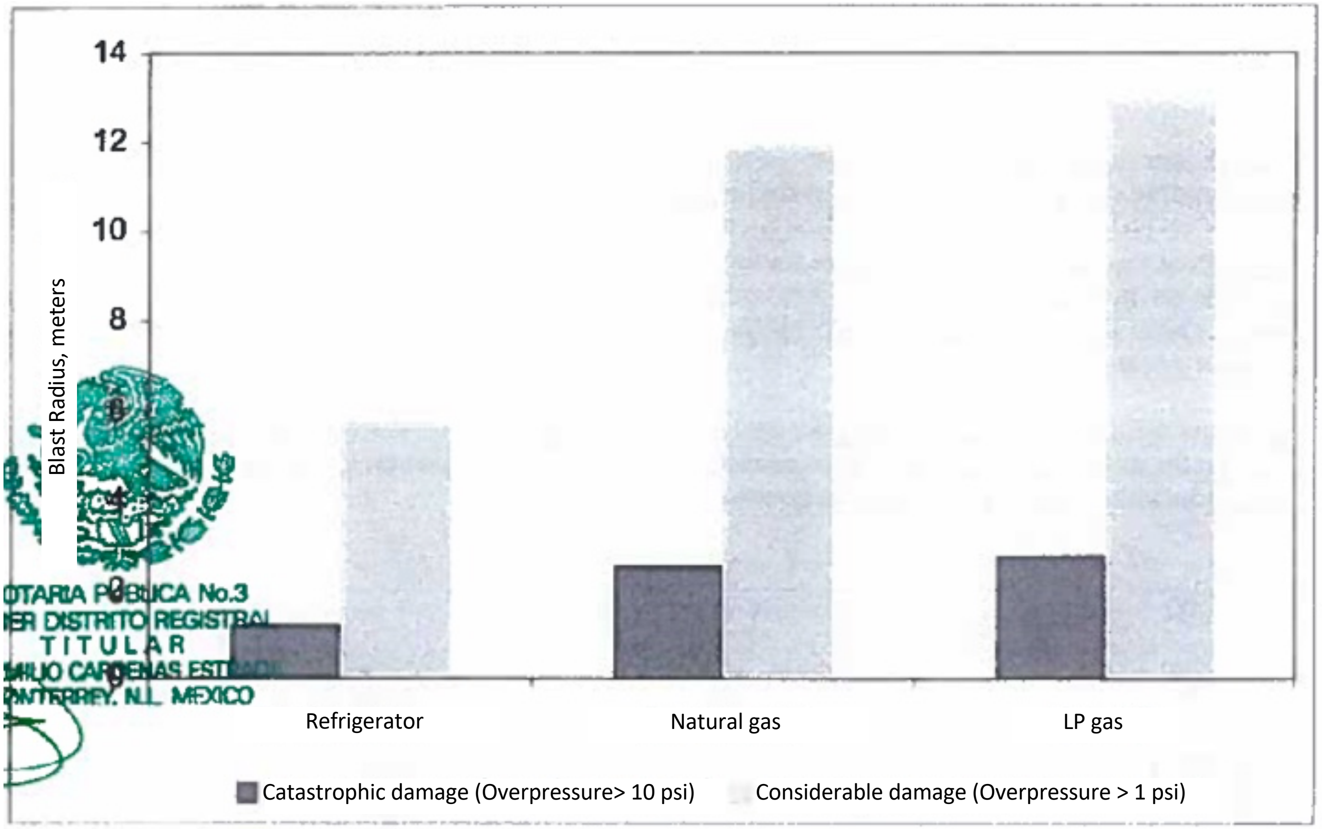

Figure 4. Blast radii for catastrophic and moderate (considerable) damage for leak and explosion events involving RHC 134 refrigerant in a household refrigerator, natural gas and LP gas coming from a leak in a residential stove.

Figure 4 shows that the explosion events caused by natural gas and LP gas leaks are similar to each other, and that the corresponding blast radii, compared to a leak of refrigerant, are approximately double in magnitude.

Case 4: Chiller-type equipment for cooling water used in air conditioning or industrial cooling systems.

Refrigeration equipment such as that considered in this case operates with a closed circuit of cooling water (or another substance depending on the desired temperatures). The function of the chiller is to keep the water cooled to the correct temperature in order for it to be flowed through tubing to the cooling equipment (air cooling equipment, for example, in air conditioning applications) in the various areas. Once the cooled water exchanges heat in the equipment, the water returns to the chiller to again bring it to the correct temperature. Chiller equipment is typically installed on a rooftop where water cooling operations are performed for the cooling-chiller circuit. Typical applications for these systems are industrial or commercial. In these systems, the condenser as well as the evaporator (heat exchanger between the refrigerant and the cooling water) are located in the same area, commonly outdoors on the roof of the building.

The chiller equipment considered in this assessment of risks uses 50 Kg of HCR 410 refrigerant and the potential leak and explosion event for this material will be compared to LP gas leak and explosion events in stationary 120 L (small) and 300 (industrial-commercial size) tanks. Since this type of installation

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may be industrial, the case of an acetylene leak and explosion involving a 40 Kg cylinder of the type used for welding equipment was also compared.

Due to the fact that this type of installation does not have refrigerant gas that circulates into the air conditioned areas, there is no risk of a refrigerant gas leak occurring inside, and therefore the presentation of refrigerant concentrations in the air that exceed the IDLH level.

Figure 5 presents the results of simulated leak and explosion events in the cases specified above. The catastrophic and moderate (considerable) blast radii for the explosion event are presented in each case.

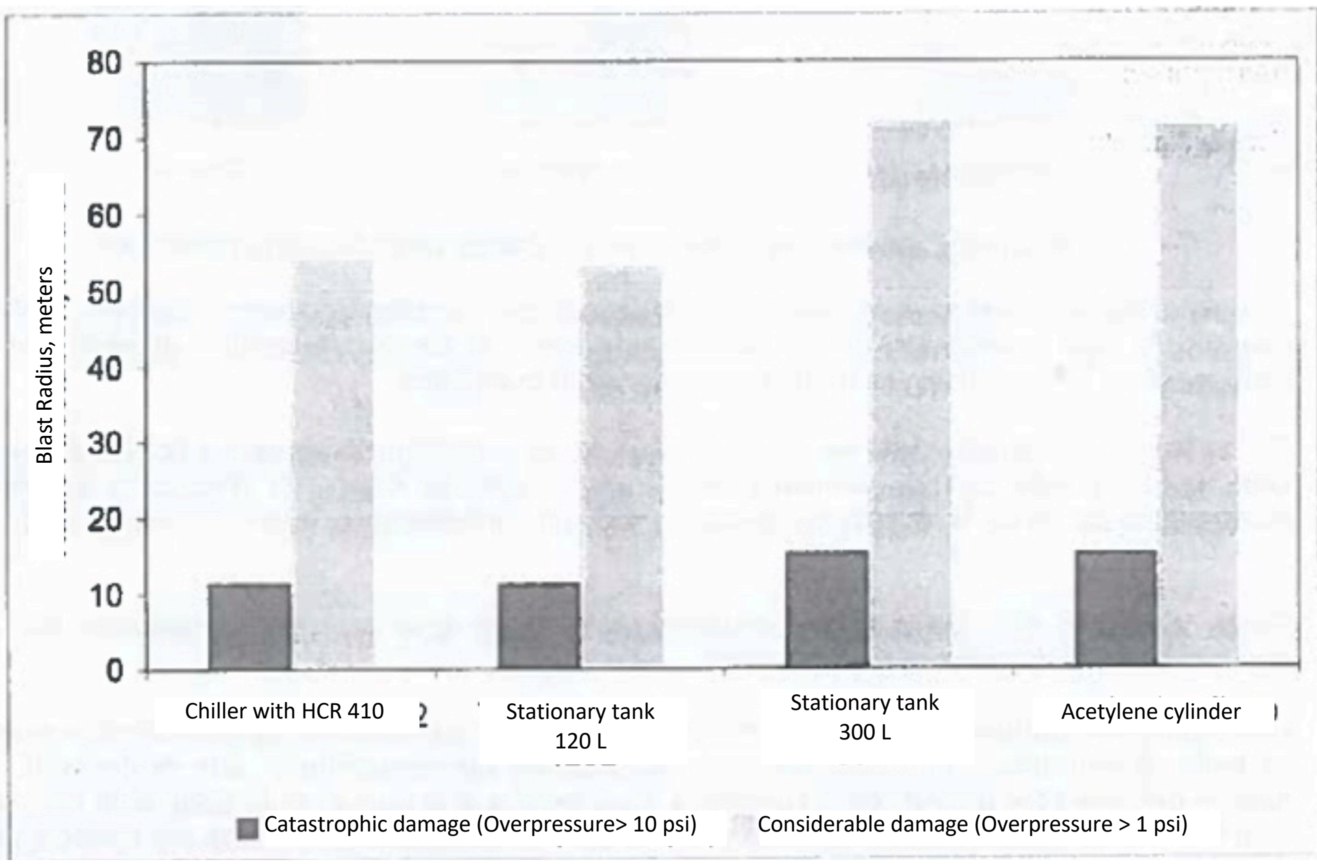

Figure 5. Blast radii for leak and explosion events: Chiller equipment with 50 Kg of refrigerant. Stationary 120 L and 300 L tanks holding LP gas, and 40 Kg acetylene cylinder for welding equipment.

Figure 5 shows that the blast radii for all these scenarios are very similar. This is due to the fact that quantities of gas (by weight) in each of the cases are also similar, and it is this factor that primarily affects the power of an explosion involving substances that have combustion heat levels that are also very similar. For chiller cooling equipment and for stationary LP gas tanks, the typical installation is for them to be outside, in a well-ventilated location (most frequently on the roof of the building), therefore a gas leak event will only with difficulty reach explosivity levels. This is not the case for an acetylene cylinder for welding and cutting, which is commonly used in enclosed or not-so-well ventilated areas and where the possibility of having a leak event with explosion is considerably greater due to the conditions for use.

Case 5: Equipment with 2 HP capacity for cold room refrigeration

The refrigeration equipment considered in this case consists of an enclosed, (preferably) thermally insulated room, where the refrigeration system evaporation unit will be installed. The condensation unit is installed external to the cold room, typically in a machine room.

For the equipment cooling capacity under discussion, the cold room area is between 10 and 16 m^2, with a height of 2.5 m. For the purpose of simulating risk [illegible], we will consider a 10 m^2 cold room, since this represents the worst case, having the smallest volume/ The volume of this cold room may be calculated as [illegible] m^3.

Refrigeration equipment such as that considered in this case operates using 2 kg of HCR 410 refrigerant from Panama Green. With this quantity of refrigerant, the volume necessary to achieve IDLH concentrations and the Lower Explosive Limit (LEL) in the event of a leak may be calculated. The volume necessary to achieve an IDLH of 2100 ppm is 395 m^3, while the volume necessary to reach the Lower Explosive Limit (LEL) (2% v/v) is 41.5 m^3. As may be noted, in both cases the volume necessary exceeds the volume available in the cold room, therefore in the event of a total leak of refrigerant from the evaporation system, the concentrations in the room exceed the IDLH and the LEL.

In the event of a leak from the condensation system (external to the cold room), whether the IDLH and LEL levels are reached will depend on the space available and the ventilation in the area.

Based on the foregoing information, the total refrigerant leak event with explosion is simulated, to obtain an estimate of the areas to be potentially affected. Considering that these types of installations are primarily located in commercial or industrial facilities, and for purposes of comparison, leak and explosion scenarios were also analyzed for a stationary 120 L (small size) LP gas tank), a 30 Kg LP gas cylinder, and a 40 Kg acetylene cylinder for cutting and welding equipment.

Figure 6 presents the results obtained for the explosion blast radius for the aforementioned scenarios. The figure presents the radii for catastrophic damage (overpressure greater than or equal to 10 psi) and considerable damage (overpressure waves greater than 1 psi).

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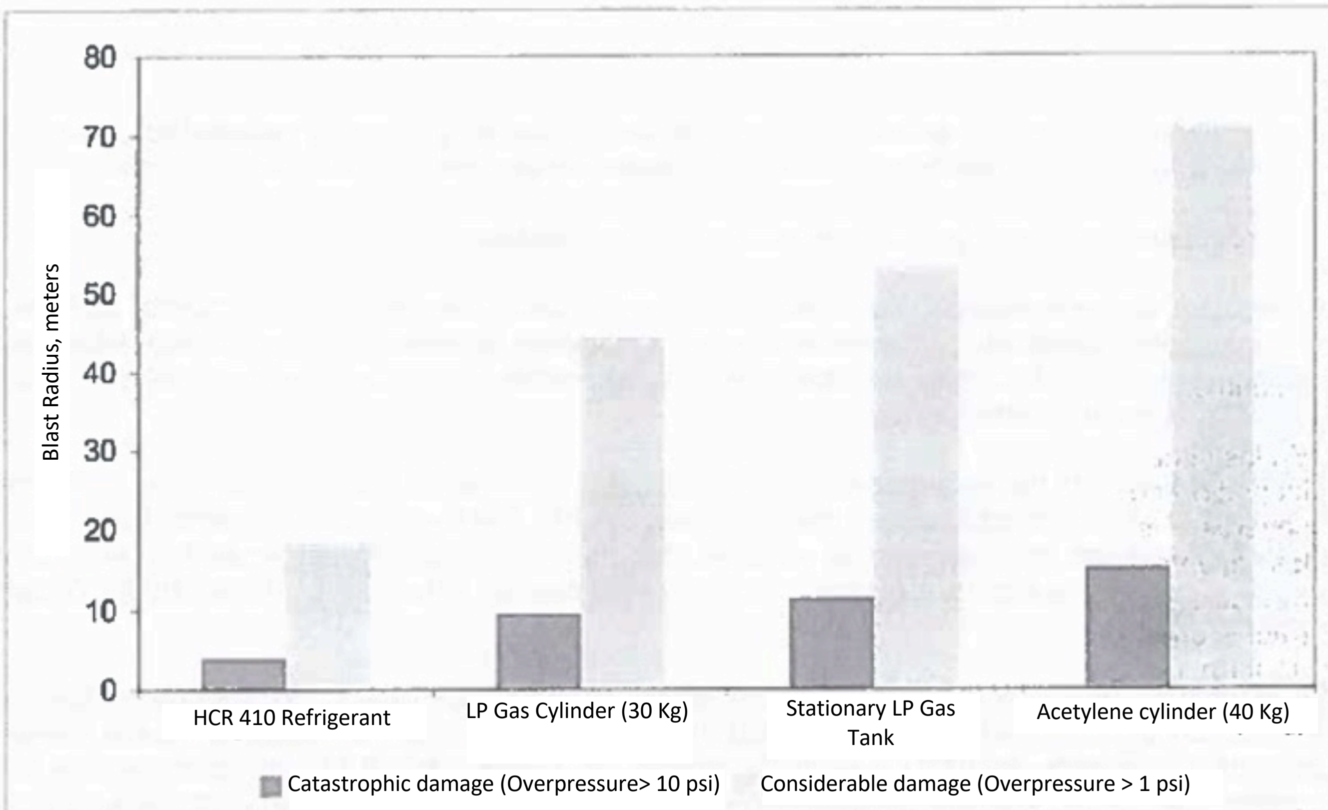

Figure 6. Blast radii for leak and explosion events involving: HCR 410 refrigerant in cold room equipment, a 30 Kg LP gas cylinder, a stationary 120 L LP gas tank and a 40 Kg acetylene cylinder for cutting and welding equipment.

Figure 6 shows that leak and explosion events involving the stationary 120 L LP gas tank, the 30 Kg LP gas cylinder and the 40 Kg acetylene cylinder have blast radii that are significantly greater than those predicted for an explosion involving the refrigerant gas used in the cold room. By way of comparison, the 30 Kg LP Gas cylinder has a radius a little greater than two-times that of the refrigerant case. Similarly, the stationary tank case yields a radius approximately three-times greater than that of the refrigerant, and the case of an acetylene cylinder yields a blast radius approximately four-times larger.

It is important to stress that of all the cases analyzed, the cold room is the only case in which the lower exclusivity limit (in the event of a leak from the evaporator within the cold room) is achieved, given the space into which the refrigerant leaks. Therefore, actions must be considered that are intended to detect and ventilate gas in a timely manner in the event that this type of leak occurs. This may be achieved by using safety devices as part of the refrigerant system itself, and within the cold room. Given that there is the possibility of having an explosive atmosphere within the cold room, the appropriate electrical and lighting facilities must be used within the cold room.

Results of the overall assessment of fire events

Potential effects of a fire event in the various facility studied we're compared against fire events for the baseline cases. In all cases, a leak of material and formation of a cloud that reached the Lower Explosive Limit were considered, thus creating an explosion of the material and the respective formation of a fireball.

It is worth mentioning that in all the proposed scenarios, except the case of a leak of refrigerant within the cold room, refrigerant concentrations in the air do not reach the LEL, therefore an explosion and fire event are relatively improbable. Nevertheless, given that specific situations may arise in each facility where the leaked refrigerant could be involved in the formation of a fireball, the effects of this event were simulated, and the distances impacted by the fire were reported.

In the simulations conducted to determine the fire burn and fireball blast radii, the buffer zones, high-risk and [illegible] damage zones were estimated. These results may be consulted in Appendix 2. To facilitate comparison of the simulated events, Table 3 presents the distances for the high-risk zones (heat radiation greater than or equal to 9.5 kw/m^2), the moderate risk zone ([illegible] of 4 kw/m^2), and the estimated length of the fireball event (stated in seconds).

Table 3. Results of simulations for fire event: Fireball

REFRIGERANTS					
Equipment	Refrigerant	Weight (Kg)	9.5 kW/m^2 High-risk distance (m)	4 kW/m^2 Mod-.risk distance (m)	Length of event (sec.)
Refrigerator	RHC 134	0.06	5.69	8.89	0.2
Mini Split 2T	HCR 410	1	13.9	21.8	0.5
Central Air 5T	HCR 410	2.5	18.5	29.1	0.5
Cold Room, 2 HP	HCR 410	2	17.3	27.1	0.5
Chiller, HCR 410	HCR 410	50	47.9	75.6	1.7
COMBUSTIBLE GASES					
Equipment	Substance	Weight (Kg)	9.5 kW/m^2 High-risk distance (m)	4 kW/m^2 Mod.-risk distance (m)	Length of event (sec.)
Acetylene Cylinder	Acetylene	40	43.7	69	1.5
LP Gas Cylinder	LP Gas	30	38.9	61.6	1.4
120 L Stationary Tank	LP Gas	64.8	49.6	78.6	1.8
180 L Stationary Tank	LP Gas	97.2	56.4	89.4	2.1
300 L Stationary Tank	LP Gas	162	66.3	105.2	2.5

Figure 7 presents a graph showing the high-risk distances determined for simulation of the various fire risk scenarios.

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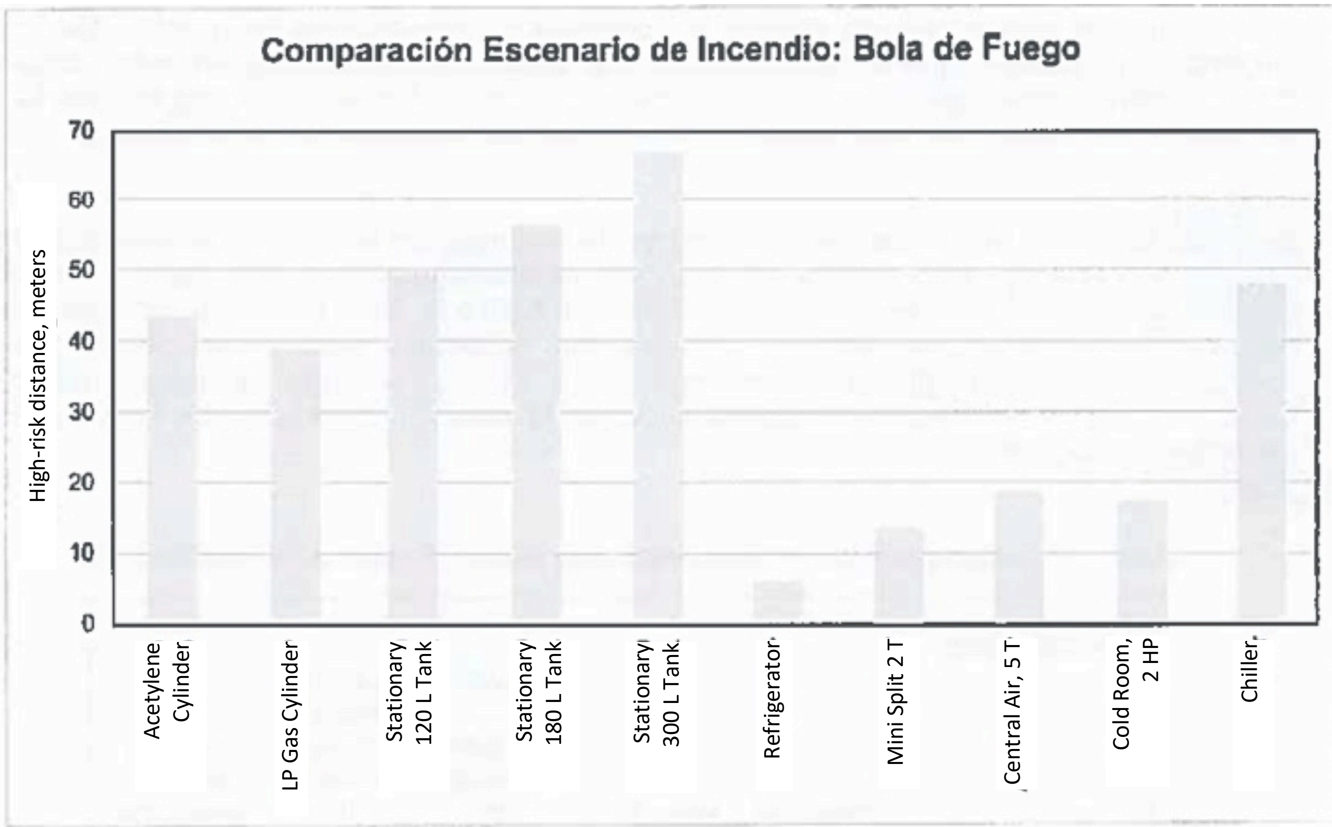

Figure 7 Distances with radiation of 9.5 kw/m^2 (high-risk) for fire events involving a fireball produced by a total leak of combustible material.

Figure 7 shows that the high-risk radiation distances for refrigeration equipment, except for chiller-type equipment, are significantly less than the distances for events involving common combustible gases. The chiller-type equipment presents a considerable distance due to the fact that it contains a significantly greater volume of refrigerant than the other equipment types. Nevertheless, since this equipment (chillers) are installed outdoors and with good ventilation, it is improbable that refrigerant would accumulate and form an explosive cloud such as that used in the simulation. This same case applies to stationary LP gas tanks, but it is possible that it would not be applicable in the cases of combustible gases stored in cylinders (LP gas and acetylene).

Conclusions and Recommendations

The primary conclusions and recommendations obtained from an analysis of the results of this study, with respect to the risks present in refrigeration systems using natural refrigerants and the comparison of the magnitude of these risk events to situations and facilities commonly located in settings where refrigeration equipment is used are presented below.

Conclusions

The primary conclusions obtained from the analysis of the cases studied are presented below, along with comparison to the baseline cases for situations commonly found in the studied facilities.

a) In the case of a total leak of natural RHC 134 refrigerant used in a household refrigerator with an 18 cu. ft. capacity, concentration levels of refrigerant that would present a health risk (based on the IDLH value) or a risk situation due to the presence of an explosive atmosphere (LEL) are not achieved. Furthermore, in simulation of an explosive event or fire involving leaked material, the resulting blast radii are considerably less than the radii for a leak event involving a kitchen stove. Based on this information, we may conclude that the use of this type of refrigerant in a household refrigerator does not introduce a major risk into the residence, compared to the risks already present, such as the presence of a gas stove in the kitchen.

b) In the case of the 2 T Mini Split air conditioning equipment, it was shown that a total leak of refrigerant from the evaporation unit (within the residence) may cause refrigerant concentrations in the air that would exceed the IDLH value, however this does not present a direct risk to health, since the materials involved are not listed as toxic. Additionally, for the case of an explosion of leaked material, it was determined that the concentrations generated by a possible leak do not reach the Lower Explosive Limit (LEL), therefore an explosion and fire event is improbable. Furthermore, the blast radii were calculated for an explosion and fire event for this case, with the result that these distances are 20 and 37% less than the distances observed for a leak and explosion event involving a household heater using natural gas or LP gas (respectively).

   For this same equipment, but in a condensing unit (installed on the roof of the building), no toxicity or explosion problem is anticipated, due to the fact that the equipment is installed in a well-ventilated area, thus the IDLH (health risk) or LEL (explosion risk) concentrations are not reached. In any case, an explosion and fire event involving the refrigerant material in a condenser unit was evaluated and compared to leak, explosion and fire scenarios involving LP gas in a stationary 120 L tank and in a 30 Kg LP gas cylinder. It was shown that for an explosion event, the blast radii for LP gas were between 3 and 4 times greater than those in an explosion event involving the refrigerant. Similarly, the impact distances for a fire event in scenarios involving natural gas were 2.7 and 3.6 times greater in the case of a 30 Kg cylinder and the stationary tank, respectively. Based on these results, it is not believed that the use of

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HCR 410 refrigerant in the 2 T Mini Split equipment presents a greater risk than those already present in a residential dwelling.

c) With respect to the scenario involving 5 T central air conditioning system equipment, it was discovered that in the event of a refrigerant gas leak that would enter the interior of the cooled area through ventilation ductwork, it is possible that the NIOSH-recommended levels based on the IDLH parameter would be exceeded. Again, this does not necessarily imply a situation that presents health risks, since the components of the refrigerant are not classified as toxic substances. With respect to the possible effects that a refrigerant gas leak would generate in an explosion and fire event, the blast radii for these events were compared to those that would be produced by a leak and explosion of LP gas from a stationary 180 L facility and for an 30 Kg LP gas cylinder, with the result that the latter two scenarios have blast radii resulting from the explosion and fire that are from 2 to 3 times greater than the effect produced by the explosion and fire events involving the refrigerant. In addition, if the refrigeration unit is typically installed on the roof of the building, outdoors, the probability of the concentration of refrigerant gases creating an explosive environment decreases considerably.

We may conclude in the case of central air conditioning equipment that the use of natural refrigerants does not present a risk greater than the risks commonly present due to the other type of equipment (e.g. tanks of combustible gas).

d) In the case of chiller-type cooling equipment, since the equipment has no refrigerant gas circuit that travels to the air cooling units within the building, there is no risk due to a leak of refrigerant gas within the cooled areas. Installation of this type of equipment in open, ventilated areas favors any leak of refrigerant occurring in the area of the equipment being diluted into the air, making it improbable that explosive conditions would be achieved. Furthermore, and to be consistent with the comparisons to commonly used equipment, the effects of the formation of an explosive cloud of refrigerant from the unit were simulated, and they were compared with leaks of LP gas from stationary tanks having a capacity of 120 L and 300 L, as well as a leak of acetylene from a 40 Kg cylinder like those used in cutting and welding systems. The blast radii the explosion and fire events in the latter scenarios were 1.4 times greater than for the case involving refrigerant, except in the case of the stationary 120 L tank, in which the effects were very similar. Based on this information, we may conclude that although the chiller cooling equipment uses a considerable quantity of refrigerant (50 Kg), it does not present a risk greater than that presented by a stationary tank holding 120 L (a small tank) of LP gas.

e) For cold room equipment with a capacity of 2 HP, it was shown that the cold room volume allowed refrigerant concentration in the air to be achieved that exceeded the IDLH value (an environment not recommended for health reasons) as well as the LEL (explosive environment), in the event of a refrigerant gas leak from the evaporator unit. Risk events involving a leak of refrigerant gas and the subsequent explosion and fire were simulated, and the results obtained were compared with the leak, explosion and fire scenarios for a 30 Kg LP gas cylinder, a stationary 120 L LP gas tank and a 40 Kg acetylene cylinder for cutting and welding equipment. The results showed that the impact distances for the explosion and fire events subsequent to a refrigerant gas leak were between 2.4 and 4 times less than the impacted radii for the same events in the scenarios involving LP gas and acetylene. This means that the use of natural refrigerant gas in cold room equipment does not present a risk any greater than the risks present in common installations, such as LP gas tanks or the presence of gas cylinders used for cutting and welding equipment.

As a general conclusion to this study, it may be stated that the use of natural hydrocarbon-based refrigerants does not present a risk any greater than the risks commonly present in the various areas where these refrigerants are used: residential, commercial or industrial settings. Nevertheless, the presence of refrigerants with flammability properties such as those of natural hydrocarbon-based refrigerants requires that equipment and facilities comply with safety and risk communication measures that are appropriate to the handling of combustible gases.

Recommendations

Although the objective of this study is not to create recommendations for the use of natural refrigerants, during analysis of the proposed scenarios, situations were identified that must be considered for the various applications of these refrigerants:

a) The use of refrigerant gases that have flammability properties in equipment where inflammable substances are not traditionally used (conventional refrigerants) requires appropriate marking and communication of the risks involved, so that the user of this equipment will be aware of the presence of flammable materials, and so that they will follow the instructions for proper use of the unit. This may avoid situations arising that would create the scenarios proposed in this study. Thus, this type of equipment may be used with refrigerants that are more environmentally friendly, with the same degree of trust as with common equipment and devices, such as a stove, a gas furnace or a hot water heater.

b) Refrigeration units that are located outdoors must preferably be installed in open, well-ventilated areas. This practice radically decreases the risk of an explosion event occurring due to a possible refrigerant leak. For example, how frequently do we hear of an explosion of a stationary gas tank? These are exceedingly rare events, even in facilities that undergo nearly zero maintenance for many years. The reason is that most of these tanks are installed on rooftops, in the open air where any amount of gas that may leak is quickly dispersed into the environment without severe consequences in most cases.

c) For the specific cases of central air conditioning and the 2-ton Mini Split equipment, there exists the possibility that, if the refrigerant leak occurs into the building, refrigerant concentrations may be reached that exceed the IDLH value. Although the IDLH value for non-toxic gases such as these is not a parameter that signals a toxicological risk situation, it is helpful to consider adequate ventilation of climate-controlled areas in order to avoid any possible problem.

d) In the case of cold room equipment, we were able to determine that within the cold room, refrigerant gas concentrations that exceed the IDLH value, and in particular, that are within explosivity limits, could be attained in the event of an evaporator leak. In this case, it is helpful to consider installation that is explosion-proof within cold rooms,

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and to consider including leak or explosive environment detection equipment. The purpose of this is to be able to properly react in the event that a leak occurs within the cold room.

THIS DOCUMENT IS A REPRINT OF THE ORIGINAL REPORT DELIVERED TO PANAMA GREEN INNOVATIONS ON JUNE 10, 2009. THE TECHNICAL OFFICIAL RESPONSIBLE FOR PREPARING THIS REPORT WAS DR. ENRIQUE ORTIZ NADAL, PROFESSOR IN THE DEPARTMENT OF CHEMICAL ENGINEERING AT ITESM, MONTEREY CAMPUS. THE REPORT COMPRISES A TOTAL OF 113 PAGES, INCLUDING THE BODY OF THE REPORT AND APPENDICES.

PREPARED BY:

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DR. ENRIQUE ORTIZ NADAL

[seal: “United Mexican States”]

IN THE CITY OF MONTERREY, STATE OF NUEVO LEÓN, UNITED MEXICAN STATES, on October 25, 2010, there appeared before me, Lic. **EMILIO CARDENAS ESTRADA,** Civil Law Notary, Regular Official of Civil Law Notary Office No. 3, for the First Registry District in the State, Regular Official of Civil Law Notary Office No. 3, **Mr. ENRIQUE ORTIZ NADAL,** who **REPRESENTED:** That he approved the entire content of the foregoing TECHNICAL REPORT titled, “Comparative risk Study for Natural Refrigerants”, which he prepared, in his capacity as Professor in the Department of Chemical Engineering at ITESM, Monterrey Campus, for ECOFREEZE INTERNACIONAL, S.A. de C.V., which he recognizes as his own and which he signed with his own hand on Page 26 of the aforementioned Technical Report.

BACKGROUND INFORMATION:

Mr. **ENRIQUE ORTIZ NADAL,** who was identified by Voter I.D. No. 104222389299, issued by the Federal Elections Institute, and who stated that he was Mexican by birth, of legal age, married, a native of Córdoba, Veracruz, where he was born on May 22, 1966, a Professor, current in payment of his Income Tax, without verification at the moment, holder of Federal Register of Taxpayers (RFC) No. OINE-660522-VE2, domiciled at Avenida Eugenio Garza Sada No. 2501, South, in Colonia Tecnológico, in this city of Monterrey, Nuevo León, Mexico.

I HAVE ACKNOWLEDGED THE FOREGOING, for the relevant purposes stated by law, acknowledging this Ratification in the Non-Protocol Copybook at No. 126,142/2010. IN WITNESS WHEREOF.

[illegible signature]
LIC. EMILIO CARDENAS ESTRADA
Civil Law Notary No. 3
CAEE-480312-AF9

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Apostille No. 7076/10
October 26, 2010

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Mexico

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Apostille
(Convention of La Haye of 5 October 1961)

Fees: $279.00
Sequential No.: 7076/10

In Mexico, this public instrument was signed by Lic. EMILIO CÁRDENAS ESTRADA, **in his capacity as** REGULAR CIVIL LAW NOTARY OFFICIAL No. 3 FOR THE FIRST REGISTRY DISTRICT OF MONTERREY, NUEVO LEÓN, MEXICO

This public instrument bears the seal corresponding to CIVIL LAW NOTARY OFFICE No. 3 FOR THE FIRST REGISTRY DISTRICT OF MONTERREY, NUEVO LEÓN

Certified in MONTERREY, NUEVO LEÓN, **by** LIC. MARCELA DENISSE LEAL ALANIS, MANAGER, LEGALIZATIONS UNIT **ON** October 26, 2010

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